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Is a low-phosphorus content in steel a product requirement?

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Abstract

An attempt is made, on the basis to published literature, to assess the amount of phosphorus that might be present in the steels without making it susceptible to grain boundary embrittlement. Embrittlement occurs when the general resistance to plastic flow is comparable to the stress required to separate crystals at their boundaries. A criterion is developed that enables a simple assessment to be made of the tendency to embrittle as a function of yield strength and the fraction of grain boundary sites that are covered by phosphorus. The latter is also sensitive to chemical composition, since some elements such as carbon segregate preferentially to phosphorus, giving rise to site competition that can permit a greater tolerance to the impurity. Other solutes affect the embrittling potency by different mechanisms, not all of which are clear.

Keywords: Phosphorus, segregation, embrittlement, strengthening, steel design

1. Introduction

That phosphorus embrittles iron has been known since at least 1860: "a very small amount of phosphorus will make bar Iron brittle, so small a proportion as 0.5 per cent." [1]. Specifically, phosphorus embrittles grain boundaries, and its interactions with boundaries led to the creation of segregation models as early as 1948 [2], with the subject of temper embrittlement reviewed in 1953 [3] and on many occasions since then [4–9]. The boundaries

at which the segregation of phosphorus occurs may be between ferrite grains or austenite grains [10]. Considerable work has been done on the mechanism of embrittlement. A useful concept is that if a solute in iron has a greater reduction in energy (Δg_s) when transferred from solid solution to a free surface, than when it is similarly transferred to a grain boundary (Δg_b), then it embrittles the boundary because it becomes favourable to separate the grains [11]. Noting that both these energies would be negative for any solute that tends spontaneously to segregate, the potency to embrittle scales with the positive $\Delta g_b - \Delta g_s$. Table 1 shows in this context that phosphorus has a strong tendency to embrittle grain boundaries, and first principles calculations confirm this expectation for special low-Σ boundaries[1] [13]. Another interpretation quite effectively correlates the size misfit of the segregating atom relative to iron, against the energy required for boundary fracture [14].

Table 1: Selected segregation free energies for solutes in iron, from a compilation by Anderson et al. [11].

Segregant	$-\Delta g_b$/kJ mol^{-1}	$-\Delta g_s$/kJ mol^{-1}
Carbon	50-75	73-85
Phosphorus	32-41	76-80
Hydrogen	65-68	71-109

These studies do not establish whether any embrittlement is sufficient to induce brittle fracture. It is well known that slip and separation at grain boundaries are competing mechanisms, so that anything which makes slip more difficult will in general tend to lead to grain boundary failure [15]. Whether such failure occurs depends on the ability of the material within the grains to accommodate strain. Factors that should *enhance* grain boundary failure can be listed as follows:

a) matrix that is so strong that boundaries become the weak links;

b) low testing temperatures where the matrix is strengthened by the reduced mobility of dislocations;

[1] Σ refers to the fraction of lattice points that are common to two crystals that share a common origin and are allowed to interprenetrate and fill all space [12, e.g.]. Thus, a low-Σ boundary would, in general, correspond to a low energy boundary.

c) large grain size [16] since a fixed impurity content is then distributed over a smaller boundary area per unit volume. For the case where the total number of impurity atoms that can be accommodated at a boundary is much smaller than the concentration available, Ishida [17] used McLean's theory [18] for grain boundary segregation to derive a grain size dependence as follows:

$$\frac{x_b}{x_{b_o} - x_b} \approx \frac{\overline{x} - 3t(2\overline{R})^{-1}x_b}{1 - \overline{x}} \exp\left\{\frac{G_s}{RT}\right\} \qquad \text{for} \qquad 3t(2\overline{R})^{-1} \ll 1 \quad (1)$$

where x_b and $\overline{x}$ are the concentrations (mole fractions) in the boundary and the material as a whole, respectively, t is the boundary thickness, $\overline{R}$ is the grain radius and G_s the segregation free energy; the saturation coverage x_{b_o} is often assumed to be $x_{b_o} = 1$[2]. The intergranular fracture stress begins to decrease when the coverage of phosphorus on the grain boundaries is greater than about 0.1, thereafter decreasing from about 2300 MPa to 1600 MPa when the coverage is about 0.4 [19]. These data refer to a nuclear pressure-vessel steel, but should be of generic importance.

d) a large fraction of high energy boundaries where impurity segregation is favoured [20, 21]. Indeed, there are good reasons to introduce crystallographic textures that maximise low-misorientation or special boundaires (low Σ coincident site lattice boundaries); such boundaries are not only stronger in that they are more difficult to cleave, but also have less free volume for impurities to segregate [22] (Fig. 1).

It follows that strong steels will necessarily be more susceptible to phosphorus embrittlement. The vast majority of steel that is produced in the world has an ultimate tensile strength less than 600 MPa with ductility in excess of 25%. Such steels should be tolerant to phosphorus concentrations that would lead to severe difficulties in the case of very strong steels with strengths in excess of 1500 MPa.

[2]The mole fraction of solute in the boundary is therefore defined as a fraction of the two-dimensional atomic sites within the boundary plane.

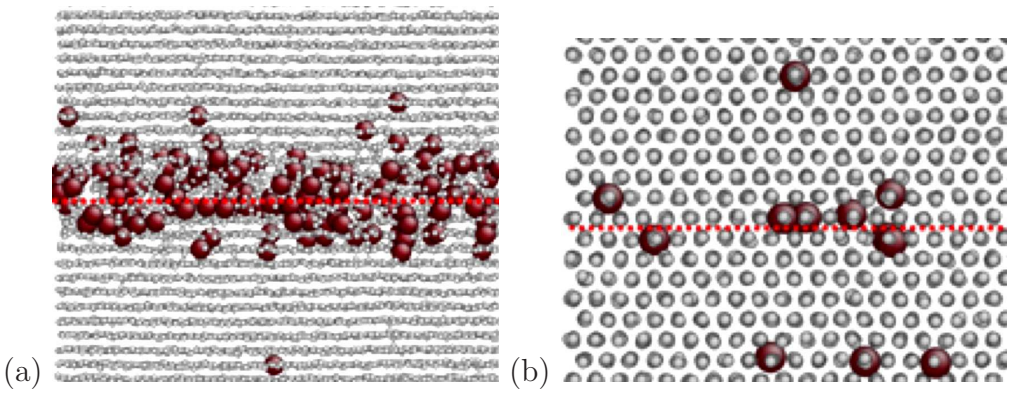

Figure 1: Simulated grain boundary segregation of phosphorus (red atoms) in Fe-0.1P at%, at 900 K. (a) High energy Σ241 boundary. (b) Low energy Σ3 boundary. Figures courtesy of Professor Byeong-Joo Lee, POSTECH.

2. Tolerable amount of phosphorus

Equation 1 derived by Ishida [17] assumes a spherical grain shape, with the size represented as a grain radius. In reality, space-filling grains approximate to a tetrakaihedron (truncated octahedron) shape, in which case the mean lineal intercept $\overline{L}$ determines the amount of grain surface per unit volume, $S_V = 2/\overline{L}$ [23] and the fraction of grain boundary to matrix volume is simply $2t/\overline{L}$. Equation 1 is therefore modified as follows:

$$\frac{x_b}{x_{b_o} - x_b} \approx \frac{\overline{x} - (2t/\overline{L})x_b}{1 - \overline{x}} \exp\left\{\frac{G_s}{RT}\right\} \qquad \text{for} \qquad \frac{2t}{\overline{L}} \ll 1 \tag{2}$$

An estimate of the average phosphorus concentration ($\overline{x}$) that can be tolerated without significantly compromising the resistance to grain boundary failure, can be made if it is accepted on the basis of experimental evidence, that properties are unaffected when $x_b \leq 0.1$. Therefore, setting $x_b = 0.1$ in equation 2, with $G_s = -34300 - 21.5 \times T$ J mol^{-1} K^{-1} [24], gives the results illustrated in Fig. 2 for realistic grain sizes. It is evident that the purity levels required at ambient temperature are not routinely achievable. There are, however, important mitigating factors. First, that the calculations are based on an assumption of equilibrium between the boundary and the matrix phases. This is unlikely at low temperatures, bearing in mind that the phosphorus must diffuse over a distance that is comparable to the grain size.

Recent calculations show that this is not likely during continuous cooling from the $Ae1$ to ambient temperatures at rates in the range 1-100 $\mathrm{K\,s^{-1}}$ [25].

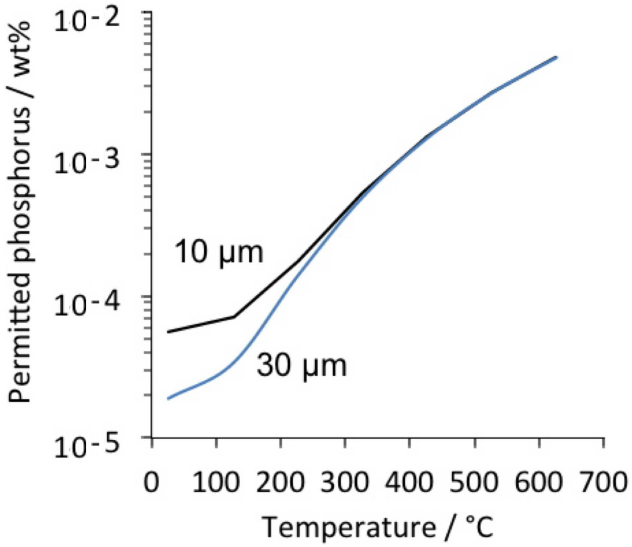

Figure 2: Given that grain boundaries are decorated by phosphorus to a concentration which is $x_b = 0.1$ of a monolayer, the ordinate refers to the average phosphorus content of the steel ($\overline{x}$) if further enrichment is to be avoided. Calculations are for an Fe-P binary alloy, with grain sizes $\overline{L} = 10\,\mu\mathrm{m}$ and 30 µm.

A second important consideration is the role of other solutes. It is known, for example, that carbon segregates to ferrite-ferrite boundaries to an extent that is two orders of magnitude greater than phosphorus [26]. This is because of its low solubility in ferrite with the atom fitting better at the more loosely packed grain boundaries. By doing so, the carbon can displace the phosphorus (Fig. 3) or limit its uptake to the boundary, thereby mitigating phosphorus embrittlement, and permitting greater quantities of phosphorus to be tolerated. Almost all structural steels contain in excess of 0.008 wt% of carbon in which case Fig. 3a indicates that carbon will occupy at least half of the boundary sites available. Fig. 3b shows that the tolerable level of phosphorus then doubles. Any element such as chromium that does not itself segregate or is prevented by low diffusivity from doing so, and which decreases the activity of carbon in ferrite will reduce the tendency for carbon to segregate and hence free up boundary sites where phosphorus can reside [24].

The site competition between carbon and phosphorus is temperature de-

pendent since the two species have different segregation energies [27]:

$$\begin{aligned} x_b^{\mathrm{P}} &= \overline{x}^{\mathrm{P}}(1 - x_b^{\mathrm{P}} - x_b^{\mathrm{C}}) \exp\left\{\frac{\Delta H_b^{\mathrm{P}}}{RT}\right\} \\ x_b^{\mathrm{C}} &= \overline{x}^{\mathrm{C}}(1 - x_b^{\mathrm{P}} - x_b^{\mathrm{C}}) \exp\left\{\frac{\Delta H_b^{\mathrm{C}}}{RT}\right\} \end{aligned} \tag{3}$$

where $\overline{x}$ represents the bulk concentration of the solute concerned, and ΔH is the enthalpy of segregation to ferrite-ferrite grain boundaries, estimated to be 50 and 80 kJ mol^{-1} for carbon and phosphorus respectively [27]. These equations do not account for grain size, but the following adaptation can be made of equation 2 for simultaneous solution:

$$\begin{aligned} \frac{x_b^{\mathrm{P}}}{[x_{b_o}^{\mathrm{P}} - x_b^{\mathrm{C}}] - x_b^{\mathrm{P}}} &= \frac{\overline{x}^{\mathrm{P}} - (2t/\overline{L})x_b^{\mathrm{P}}}{1 - \overline{x}^{\mathrm{P}}} \exp\left\{\frac{G_s^{\mathrm{P}}}{RT}\right\}, \quad [x_{b_o}^{\mathrm{P}} - x_b^{\mathrm{C}}] > x_b^{\mathrm{P}} \\ \frac{x_b^{\mathrm{C}}}{[x_{b_o}^{\mathrm{C}} - x_b^{\mathrm{P}}] - x_b^{\mathrm{C}}} &= \frac{\overline{x}^{\mathrm{C}} - (2t/\overline{L})x_b^{\mathrm{C}}}{1 - \overline{x}^{\mathrm{C}}} \exp\left\{\frac{G_s^{\mathrm{C}}}{RT}\right\}, \quad [x_{b_o}^{\mathrm{C}} - x_b^{\mathrm{P}}] > x_b^{\mathrm{C}} \end{aligned} \tag{4}$$

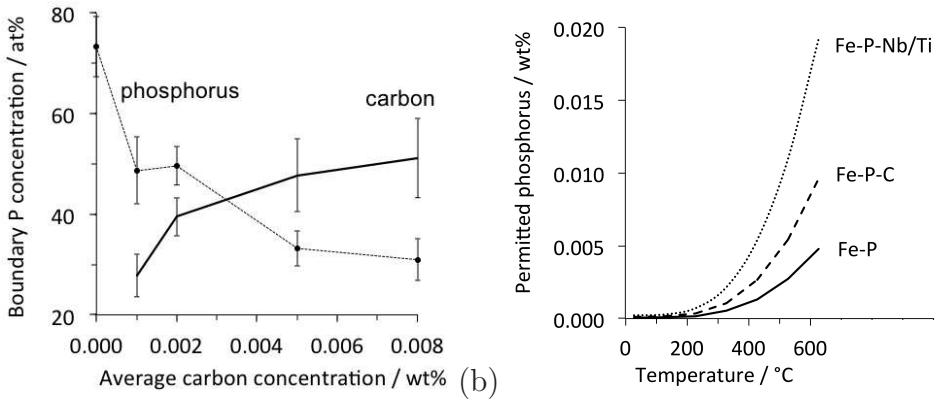

Figure 3: (a) Intergranular concentrations of phosphorus and carbon, as a function of the average carbon concentration in a Fe-0.17P wt% steels annealed at 600 °C. Adapted from [24]. (b) The grain size in all cases is $\overline{L} = 10\,\mu$m, the Fe-P line is from Fig. 2, the Fe-P-C line assumes that half the grain boundary sites are blocked by carbon, and the Fe-P-Nb/Ti assumes solute-pinning reduces the P concentration at the boundaries by a factor of four.

3. Substitutional solutes

Some alloying additions that are in solid solution have been shown to reduce the segregation of phosphorus to grain boundaries [28]. It is speculated

that this is because the alloying element has a strong chemical interaction with phosphorus, in effect pinning the phosphorus atoms within the matrix. Fig. 4 shows that both niobium and titanium reduce the phosphorus concentration at the grain boundary when ternary alloys are tempered. Titanium itself has been shown to segregate to grain boundaries and this may add to the blocking of grain-boundary sites where phosphorus might deposit. It is also possible, but not established, that titanium or niobium phosphides form, thus reducing the concentration of phosphorus available for segregation. Whatever the mechanism, Fig. 4 indicates that it is possible to achieve a four-fold decrease in the concentration of phosphorus at the grain boundaries using appropriate concentrations of niobium and phosphorus. Fig. 3b shows that in these circumstances, the tolerable level of phosphorus becomes much greater. But it is important to note that Ti and Nb are strong carbonitride formers, whereas their action in reducing the potency of phosphorus depends on their presence in solid solution.

Molybdenum undoubtedly helps mitigate the embrittling effect of phosphorus and it is argued that there is an optimum concentration that is effective in doing so (Fig 5). It is used routinely in commercial steels for the specific purpose of eliminating grain boundary embrittlement [29]. Dissolved molybdenum is said to inhibit the segregation of phophorus (scavenging), and that which segregates to boundaries acts by an unknown mechanism to improve the strength of the boundary in the presence of phosphorus [30]. Large concentrations of molybdenum become ineffective in steels due to the ready formation of molybdenum-rich carbides. The optimum concentration of Mo in the steel described in Fig. 5 is about 0.7 wt%, but this obviously must vary with the overall composition of the steel since the tendency to form carbides depends on the detailed constituents of the alloy [31].

But the story is confused. Surprisingly, molybdenum in Fe-Mo-P alloys is found not to influence the grain boundary concentration of phosphorus [32] and other experiments on steels also do not confirm a scavenging effect of molybdenum [33]. It is suggested that in Fe-Mo-C-P alloys, the formation of molybdenum carbides results in phosphorus localisation in the vicinity of the particles, but this cannot be the full explanation because convincing accumulated-experience suggests that molybdenum in solid solution dramatically reduces the tendency for failure at the austenite grain surfaces [4, 31, 34, 35]. The efficacy of molybdenum additions to counter temper embrittlement is not therefore understood, nor that of vanadium in a similar

vein.

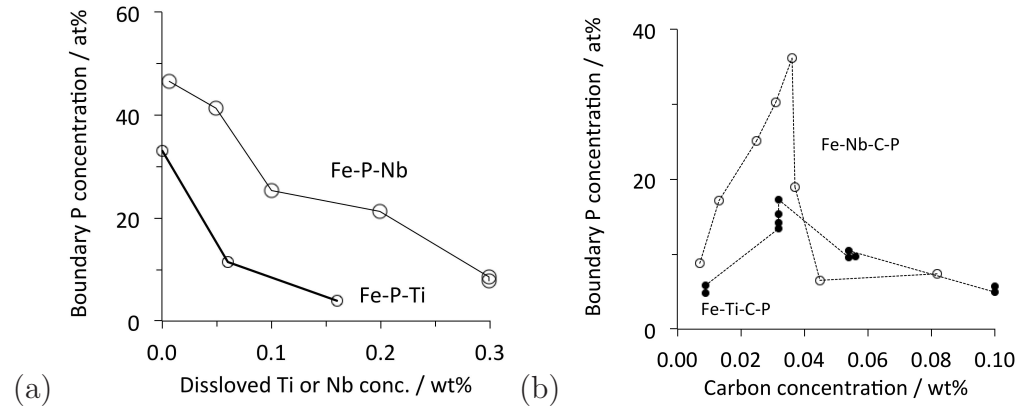

Figure 4: (a) Reduction in phosphorus segregation to grain boundaries at 550 °C, due to the presence of niobium (Fe-Nb-0.068P wt%) or titanium (Fe-Nb-0.04P wt%) in solid solution. Adapted from [32]. (b) The effect of carbon in the presence of Ti or Nb, on phosphorus segregation.

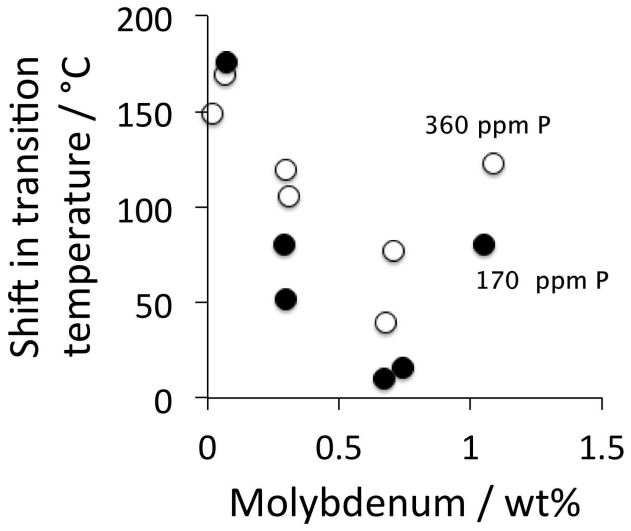

Figure 5: The effect of molybdenum in a 2.25Cr steel containing phosphorus, on the change in the ductile-brittle transition temperature. After [30].

The addition of carbon to the Fe-P-(Nb,Ti) alloys complicates things because niobium and titanium are strong carbide forming elements. Fig. 4b shows that for a fixed concentration of Nb or Ti, the addition of carbon initially increases the phosphorus concentration at the boundaries because of

the formation of NbC and TiC, thus diminishing the beneficial effects of the microalloying additions. However, at sufficiently large concentrations, the excess carbon then becomes available to block the grain boundary sites and hence reduces the tendency for phosphorus to segregate [32].

Phosphorus embrittlement phenomena in irradiated steels are extremely important in determining the long-term structural integrity of nuclear power plant components such as reactor pressure-vessels. In particular, irradiation can encourage phosphorus segregation to grain boundaries [36] through an atomic mobility that is enhanced by the creation of point defects. An interesting study in this context involves the addition of hafnium, which reduces the potency of this effect by trapping vacancies and facilitating the recombination of vacancy-interstitial pairs [37].

An alternative strategy to mitigate the effect of phosphorus is to getter it using strong phosphide forming elements such as La and Ce [38, 39]. For example, in creep-resistant steels such as the classical $2\frac{1}{4}$Cr-1Mo steel, about 0.16 wt% of lanthanum is said to relieve temper embrittlment due to 0.02 wt% P [38]. Such elements also combine with oxygen and sulphur to form oxysulphides that can be coarse and lead to a reduction in toughness. It is not clear whether the use of these elements for the purpose of fixing phosphorus has been implemented commercially, possibly because of difficulties in adding the elements to molten steel. The addition of lanthanum just before rapid solidification has been reported to successfully scavenge phosphorus [40], but such a process is for niche materials requiring compaction using powder-metallurgical techniques.

4. Influence of strength

It is has been known for some time, that temper embrittlement effects become more of an issue as the strength of the steel is increased, although surprisingly, the effect is being rediscovered in modern literature [41]. The classic behaviour is illustrated in Fig. 6; the sensitivity of the impact ductile-brittle transition temperature increases dramatically as the hardness of the steel changes from 100 to 300 HV.

This behaviour must be related to the ability of the grain interior to accommodate plastic deformation; a harder matrix will transfer the load more effectively to the grain boundaries, and hence facilitate their separation.

How can this be formulated into a quantitative model?

Naudin et al. [19] measured the prior-austenite grain boundary cleavage strength using notched tensile tests and related the data to measured phosphorus concentration (fraction of monolayer at the boundary). When the latter is less than about 0.1, failure occurs by intragranular cleavage, but beyond that phosphorus concentration, a large fraction of the fracture occurs by separation at the prior-austenite grain boundaries. The results are plotted in Fig. 7 as the dark-shaded region encompassing the uncertainties in the measured data. The presence of a notch in the tensile test would lead to constraint and a stress concentration by a factor of about three; the shaded region represents the failure stresses measured by Naudin, divided by this factor in order to represent failure in a monotonic tensile test. This correction is a little uncertain but is consistent with the fact that the measure monotonic tensile strength for the steel studied [19] at 643 MPa is consistent with the derived uniaxial yield strength in Fig. 7 for zero phosphorus.

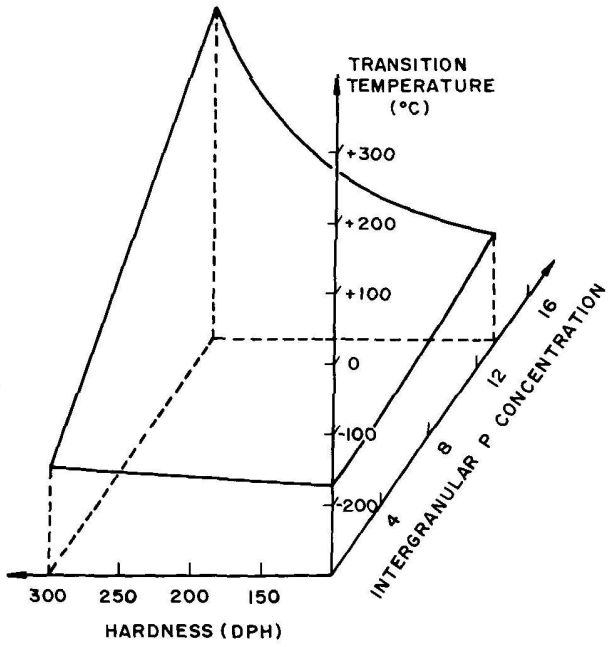

Figure 6: Dependence of the impact transition temperature on the hardness and phosphorus concentration of a particular steel (reproduced with permission from Metallurgical Transactions A, [42]). The intergranular concentration is the atomic percent of boundary sites covered by phosphorus.

Chen and co-workers [41] related the ductile-brittle transition temperature T_{DBTT} of interstitial-free steel, to its hardness H (manipulated by ageing at different temperature but keeping the ferrite grain size constant) and the

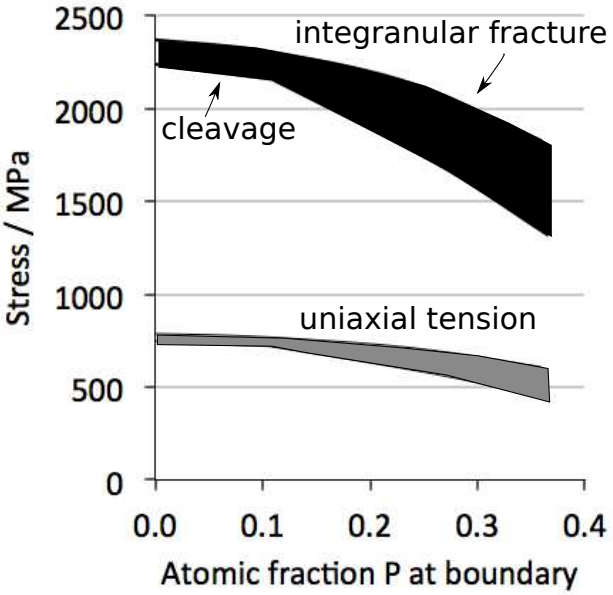

Figure 7: The upper black-region represents the cleavage strength (−60°C) for a phosphorus covers only a fraction 0.1 of the boundary, and the prior-austenite intergranular fracture stress for larger concentrations (adapted from [19]). The lower grey-region shows the same data divided by a factor of 3. Note that the concentration on the horizontal axis is not the average concentration in the steel.

atomic fraction of phosphorus x_{P} at the boundary:

$$T_{DBTT} \approx 0.24H + 1.6x_{\mathrm{P}} - 34.8 \qquad ^{\circ}\mathrm{C} \tag{5}$$

This empirical equation is specific to their study since the Charpy test is empirical, and in any case the samples used were non-standard. But it is unlikely that there should in general be a linear relationship with strength because the method takes no account of the difference in the strength of the boundaries and that of the matrix.

The grey region in Fig. 7 therefore can be used to see whether, for a given phosphorus coverage in the grain boundary, the yield strength of the material is large enough to suffer from intergranular separation. If the strength of the steel concerned falls below the level prescribed, then the matrix is able to accommodate plastic strain without transferring sufficient load on to the boundaries to cause intergranular fraction. For example, if the atomic fraction at the boundary is 0.4 then the yield strength of the steel should not exceed about 400 MPa in order to avoid susceptibility to phosphorus embrittlement.

The analysis is approximate because the fracture strength of the black region was measured at -60 °C. Therefore, it is the strength at that temperature that should be compared against Fig. 7, but such data are not readily available. A good approximation is to add 105 MPa to the proof strength used [43].

If the concept embedded in Fig. 7 is now applied to interstitial-free steels, what have a proof strength of 120-180 MPa [44] which when corrected for temperature gives 225-285 MPa, then the alloys would clearly be much more tolerant to phosphorus than stronger steels. This is why substantial quantities of phosphorus can be added without compromising ductility, because the solute is known to increase both the strength and work-hardening capacity of ferrite [45]. In galvanised versions, the segregated phosphorus reduces the tendency to form the brittle γ-Fe_3Zn_{10} phase in Fe-Zn coatings, possibly by blocking diffusion through grain boundaries [46–48], or through surface segregation of phosphorus [49]; but the consequence is that the phosphorus indirectly enhances the formability of galvanised interstitial-free steels.

Concentrations of phosphorus typically 0.05-0.1 wt% or also greater, have been reported in the literature [46, 50–55]. The steel usually also contains titanium and niobium with the primary purpose of tying up any carbon, but which additionally help mitigate the deleterious effects of phosphorus, as described in section 3. The material is produced in sheet form for the automotive industry so it is difficult to assess the potential for embrittlement as is done for pressure-vessel steels. However, deep-drawn cups that are subjected to impact deformation do reveal ductile-brittle transition temperatures, and phosphorus undoubtedly raises this [50–52, 56, 57]; an intergranular failure mechanism related to phosphorus can also manifest during fatigue loading [58]. Boron is often used to mitigate the embrittlement by occupying some of the grain boundary sites at the expense of phosphorus, or by an intrinsic grain boundary strengthening effect due to the segregated boron [50, 53, 55]. There is also clear evidence for phosphorus segregation to the α/α phase boundaries, segregation that seems impossible to avoid by rapid cooling [25].

Very large concentrations of phosphorus, approaching 0.8 wt% in interstitial-free steel alloyed with niobium leads to the precipitation of FeNbP compounds, which embrittle the steel during cold-rolling operations [59]. It has been argued [55] that when a high-strength interstitial-free steels are not required, phosphorus and boron are best avoided since they cause a decrease

in elongation, and the surface quality of the steel [60, 61].

Table 2: A few examples of phosphorus alloyed interstitial-free steels, with compositions in wt%. Not all of these alloys are commercial, many created to study the interactions between phosphorus and boron.

C	Mn	P	S	B	Ti	Nb	N	Others	Reference
0.0014	0.14	0.013	0.010	0.0001	0.037	0.005	0.0042	Si 0.01, Al 0.046	[52]
0.0016	0.15	0.17	0.011	0.0001	0.046	0.006	0.0015	Si 0.01, Al 0.053	[52]
0.002	1.50	0.10		0.0005	0.045	0.004	0.002	Si 0.01	[50]
0.002	2.00	0.10		0.0005	0.045	0.004	0.002	Si 0.51	[50]
0.002	1.50	0.15		0.0005	0.045	0.004	0.002	Si 0.50	[50]
0.0038	0.16	0.06	0.007		0.03	0.03	0.003	Si 0.50	[51]
0.0009	0.18	0.105	0.010	0.0022	0.039		0.0013	Si 0.02	[53]
≤ 0.004	1.0-1.2	0.10	0.002		0.02	0.04	0.003		[55]
≤ 0.004	1.0-1.2	0.10	0.002	0.0010	0.02	0.04	0.003		[55]
≤ 0.004	1.0-1.2	0.05	0.002		0.02	0.04	0.003		[55]

5. TRIP-assisted steels

There is a consensus that phosphorus can help increase the retained austenite content in TRIP-assisted steels that have a microstructure of allotriomorphic ferrite, bainitic ferrite and retained austenite [62]. Some chemical compositions are listed in Table 3. Concentrations up to 0.2 wt% do not seem to lead to a significant deterioration in the uniform ductility, for alloys where the yield strength is less than 600 MPa, and the ultimate tensile strength 600-950 MPa [62], although the total elongation has been shown to deteriorate [63]. There are two reasons for the apparent tolerance of TRIP-assisted steels to large phosphorus concentrations:

- the microstructure is dominated by allotriomorphic ferrite, which forms by a diffusional mechanism and hence can grow across the austenite grain boundaries. Therefore, unlike displacive transformations such as martensite and bainite where the transformation products are confined to individual grains, there are no prior-austenite grain boundaries left for phosphorus to segregate to. This makes the microstructure much less sensitive to classical impurity enhanced embrittlement.

  This is consistent with the fact that the presence of allotriomorphic ferrite in steel weld metals reduces the propensity to intergranular fracture at the prior austenite grain boundaries [64, 65].

A similar phenomenon is observed during the infiltration of prior austenite grain boundaries by liquid zinc. In a study of the heat-affected zone of steel welds, the susceptibility to liquid zinc embrittlement was reduced as the allotriomorphic ferrite content increased [66]. The absence of allotriomorphs at the prior austenite grain boundaries made them more sensitive to zinc infiltration, because the prior boundaries have a high-energy structure which is susceptible to wetting and impurity segregation.

- Secondly, the yield strength of the materials is quite low, meaning (Fig. 7) that plastic flow can prevent the onset of cleavage. Although a high phosphorus concentration in solution should permit $x_b \to 1$, the fraction of preserved prior-austenite or austenite-austenite grain boundaries in TRIP-assisted steels will be very small.

Phosphorus is said to retard the formation of cementite and stabilise retained austenite in TRIP-assisted steels [67–69]. There is no clear theoretical basis for such an effect; it is argued that phosphorus reduces the activity of carbon in cementite [70]. But this in itself is not a complete interpretation since equilibria between phases should be considered. Furthermore, studies on carburised steel [71] suggest contradictory observations, that phosphorus stimulates the formation of cementite at the austenite grain boundaries, thereby leading to a reduction in the stability of any retained austenite. This is also consistent with the Fe-C-P phase diagram that shows the emergence of cementite as an equilibrium phase when the phosphorus concentration is increased at a constant temperature [72], and with phase diagram calculations that show cementite increasing as the phosphorus concentration is raised while maintaining the temperature constant [73, Fig. 6a].

There is a danger that phosphorus concentrations in excess of about 0.2 wt% in TRIP-assisted steels may lead to Fe_3P precipitation in either the austenite or ferrite phases [74]. The consequences of such precipitation do not seem to have been established experimentally. It has been suggested in the context of automotive steels, that the crack path can preferentially pass through bainitic-ferrite interfaces containing segregated phosphorus, although the evidence provided was minimal [75].

Table 3: Phosphorus-containing TRIP-assisted steels. The composition in the case of [68] seems to be nominal.

C	Mn	Si	Al	P	other	Reference
0.18	1.33	0.45		0.006		[62]
0.12	1.58	0.53		0.068		[62]
0.14	1.57	0.53		0.204		[62]
0.2	1.4	0.5	0.7	0.04		[68]
0.15	1.60	0.30		0.07		[70]
0.13	1.38		1.55	0.055	Cu 0.46	[63]
0.13	1.45		1.66	0.100	Cu 0.48	[63]
0.22	1.50	0.44	1.34	0.073		[76]
0.19	1.50	0.25	0.44	0.015		[77]
0.22	1.54	0.27	1.75	0.018		[77]
0.18	1.50	0.26	0.44	0.102		[77]
0.18	1.83	0.48		0.076		[78]

6. Phosphorus in steel castings

Cast steels will in general contain more defects (such as porosity) and coarser chemical-segregation when compared against those that are processed subsequently by deformation. Chemical segregation exaggerates the local concentration of phosphorus in enriched regions and can compromise mechanical properties [79]. It follows that there may exist defects other than those caused by phosphorus embrittlment that can control structural intergrity, so it may not be appropriate use Fig. 7 in assessing the tolerable level of phosphorus. The mechanism of embrittlement may also differ. For example, in an investment casting, thin films of iron phosphide have been reported to form at grain boundaries even though the average phosphorus concentration was 0.009 wt% [80]; this is because slow cooling at temperatures in excess of 1400 °C led to the enrichment of phosphorus in the last liquid to solidify at the austenite/liquid interfaces. Not surprisingly, phosphorus has also been shown to be segregated in cast ingots [81, 82]. In such circumstances, macroscopic regions of castings may have significantly deteriorated properties when compared with those regions that solidify first.

Thin-slab cast steels [83–86] that are made by melting scrap do not have the advantage of substantial thermomechanical processing prior to achieving

the final product. It is found that substantial concentrations of phosphorus ($< 0.2\,\mathrm{wt\%}$) in such steel can lead to a reduction in the austenite grain size by a factor of two, because the phosphorus stabilises some δ-ferrite that pins the boundaries of the austenite grains [83, 84].[3] The argument is that such additions can be made into low-grade steels, but the detailed consequences of the effect on mechanical properties have not been reported.

7. Conclusions

Phosphorus is in general to be avoided in strong steels, but can be tolerated in larger concentrations in low-strength varieties. The following specific conclusions can be reached:

1. The strength of the steel is the largest factor of importance in determining the tolerable level of phosphorus. The plot presented in Fig. 7 can be used to assess whether the steel is likely to suffer from phosphorus embrittlement when the toughness testing is carried out at $-60\,^{\circ}\mathrm{C}$.

2. The atomic fraction of phosphorus at the boundary depends on the grain size and the presence of other alloying elements such as Nb, Ti and C in solid solution. This should be accounted for when considering the relevant location on the horizontal scale of Fig. 7.

3. According to Fig. 7, steels where the tensile strength exceeds about 750 MPa will contain significant fractions of cleavage or intergranular fracture even at relatviely small concentrations of phosphorus.

4. Equations such as 4 can be used to estimate the concentration of phosphorus at the grain boundaries when there is site competition. The data necessary for such calculations include boundary segregation energies and the concentrations of solute that are dissolved. Such equations do not of course consider kinetics, but separate diffusion theory can be implemented to estimate segregation kinetics, for example [88, 89].

[3] A corollary is that because phosphorus stabilises ferrite, an addition of 0.06P wt% to $2\frac{1}{2}$Cr1Mo steel leads to a reduction in hot ductility during hot-deformation due to the formation of a thin layer of allotriomorphic ferrite and the austenite grain boundaries [87].

Therefore, although there are no simplistic statements regarding the tolerable concentration of phosphorus, some guidelines have been established that should form the basis of a consolidated model that includes strength, test temperature, solute concentrations and possibly, strain rate as variables.

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